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Black Char and Green Char

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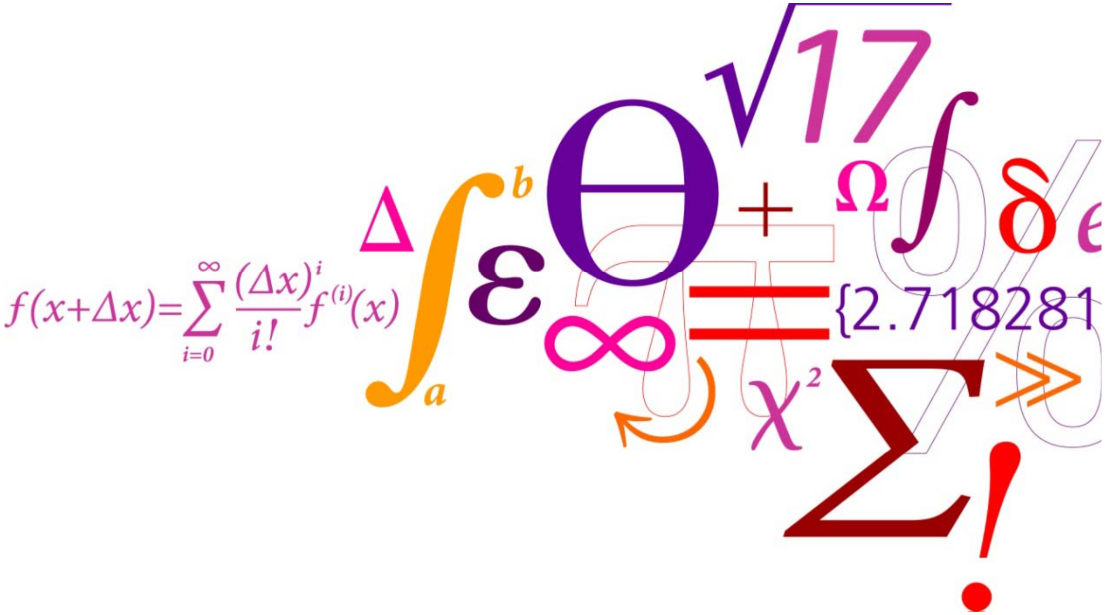


Lay out of talk

- Risø National laboratory
- Biomass gasification Group
- Applications

Lay out of talk

- Risø National laboratory
- Biomass gasification Group
- Applications

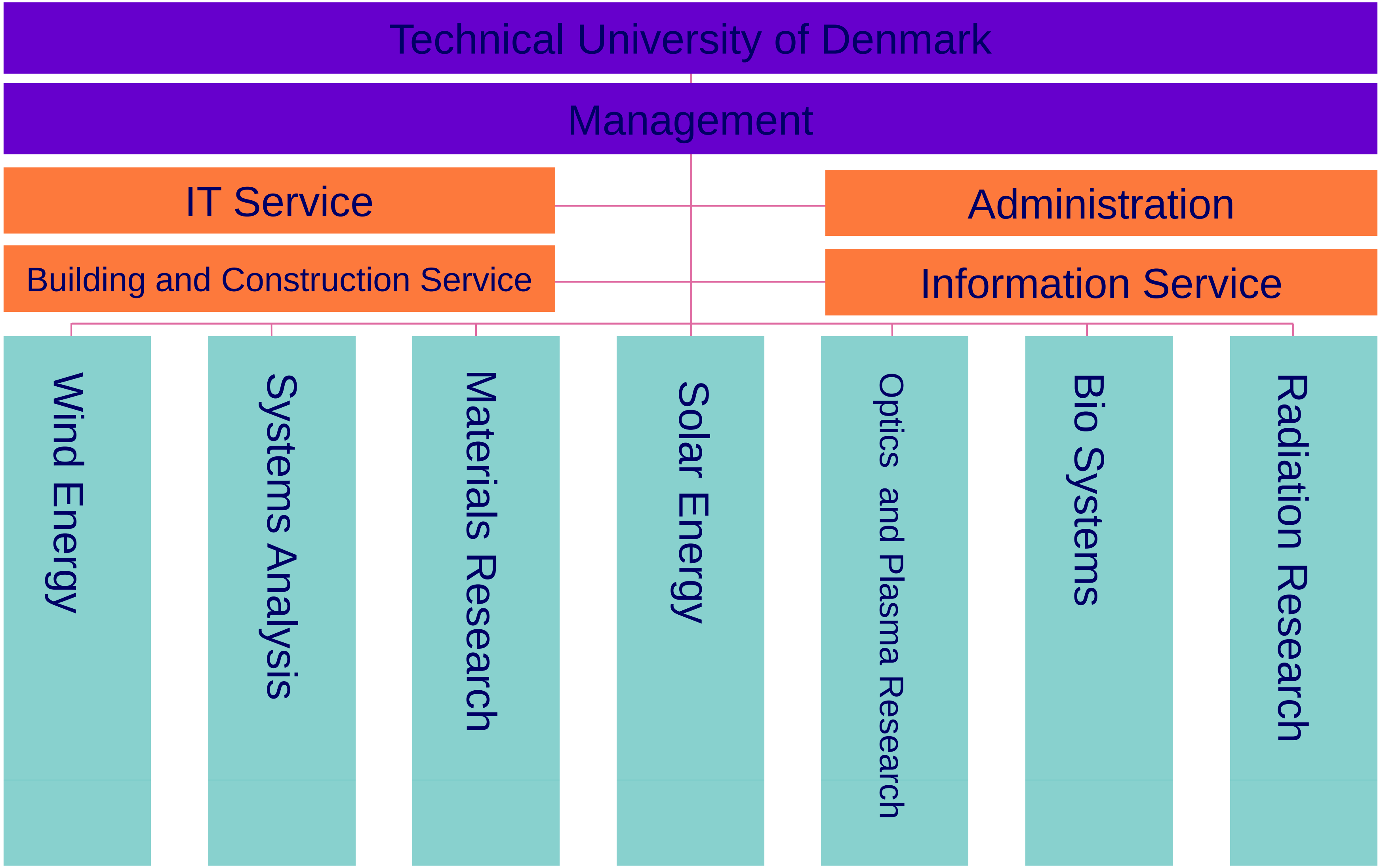
National Laboratory for Sustainable Energy

www.risoe.dtu.dk

Risø's history in brief

- **1956** Object: Peaceful utilization of nuclear energy
- **1976** Object: Nuclear energy and other energy sources
- **1986** Object: Energy
- **1990** Object: Technological research and development with energy as main focus area
- **1994** State-owned enterprise
- **2000** The last nuclear reactor is decommissioned
- **2007 merged with the Technical University of Denmark**

Organisation



Biomass Gasification Group

Research Areas

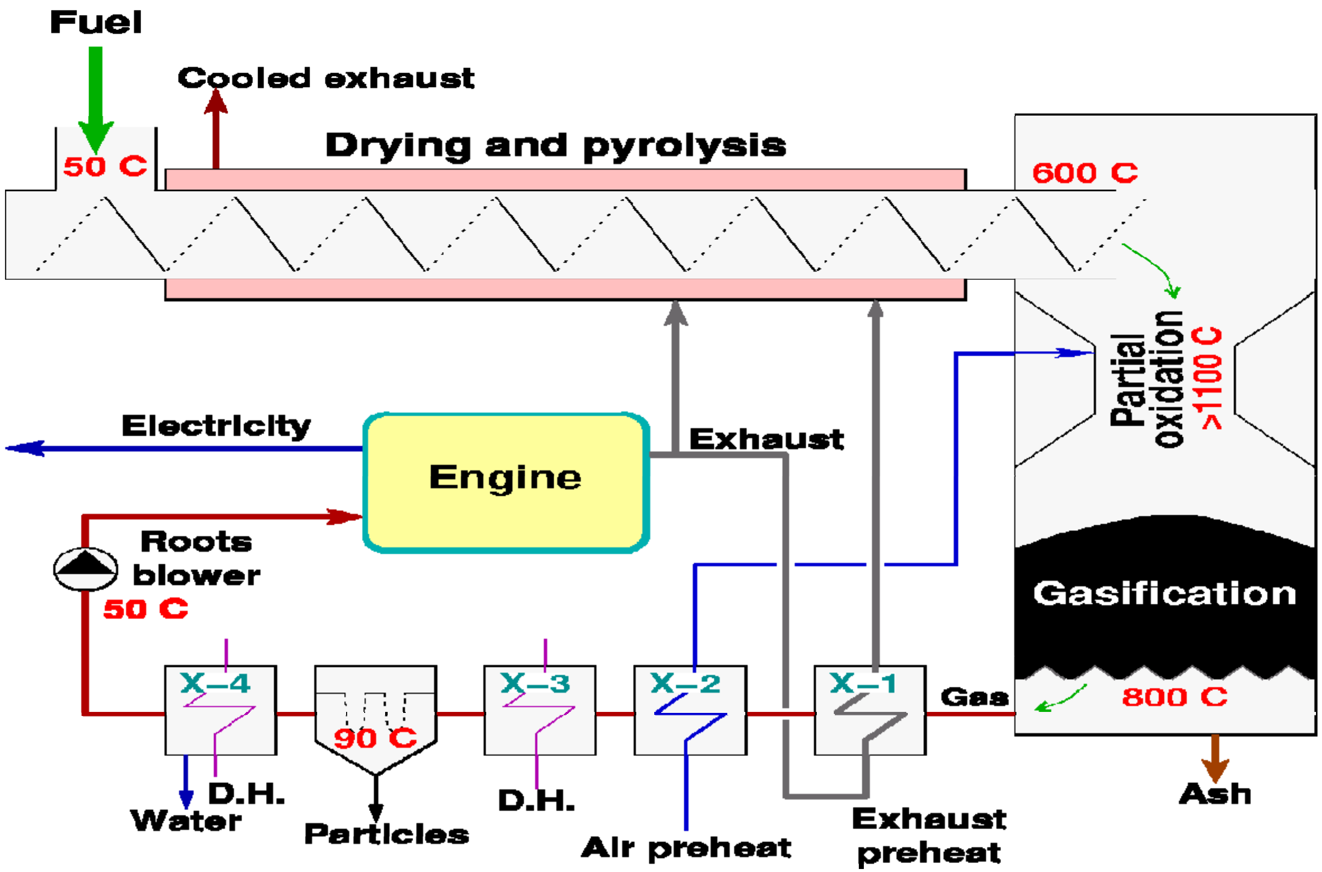
- Gasification processesTwo-stage fixed bed gasification (Viking)
- Low temperature fluid bed gasification (LT-CFB)
- Pyrolysis processes
- Gas cleaning
- Particle filtration
- Tar reduction through partial oxidation and tar char reactions

Thermal Gasification at Risø DTU

The Viking TwoStage Gasifier

Thermal Gasification at Risø DTU

The Viking TwoStage Gasifier



New Research Areas

Torrefaction of Biomass and Waste

Torrefaction is a new thermo-chemical pretreatment primarily used for upgrading the fuel properties of biomass.

The process is characterized by an operating temperature of 200 – 300 ^{o}C, absence of oxygen and low heating rates.

New Research Areas

Fundamental Understanding of Pelletization

Objectives:

- **Flexible and effective utilization of biomass as fuel**
- **Standardised fuel with clean burning properties**
- **Upgrading of waste residues to high value fuel**
- **New knowledge in the border area between energy engineering and wood science**

On the chemistry of char

An isotope study

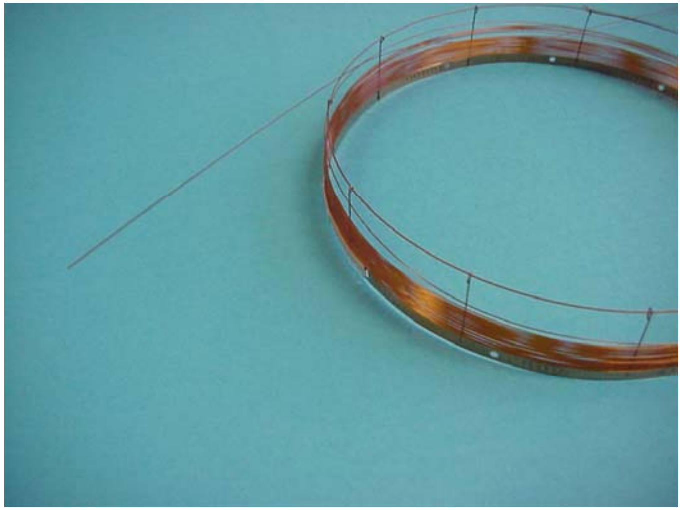
The potential of isotopes in chemistry

Isotopic labelled compounds are close to the ideal chemical internal standard

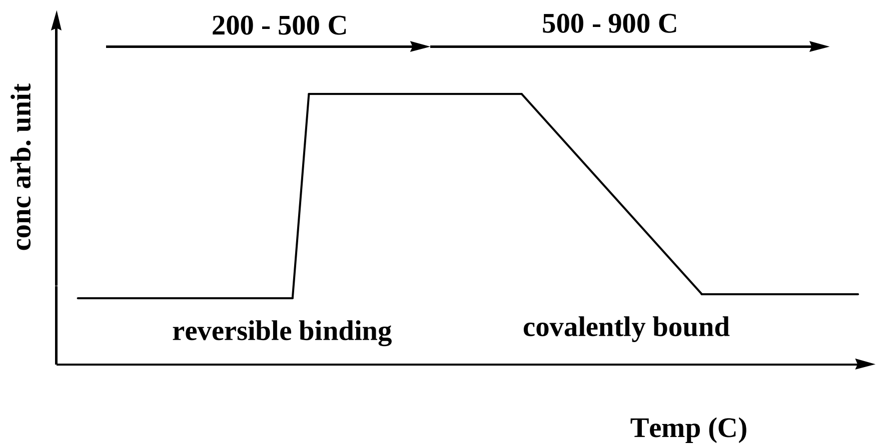
Isotopes may be used to disclose hidden reactions

- **Tracer studies**
- **Fine variations in the natural abundance of isotopes**

Analysis by GC/MS



Reactivity of char

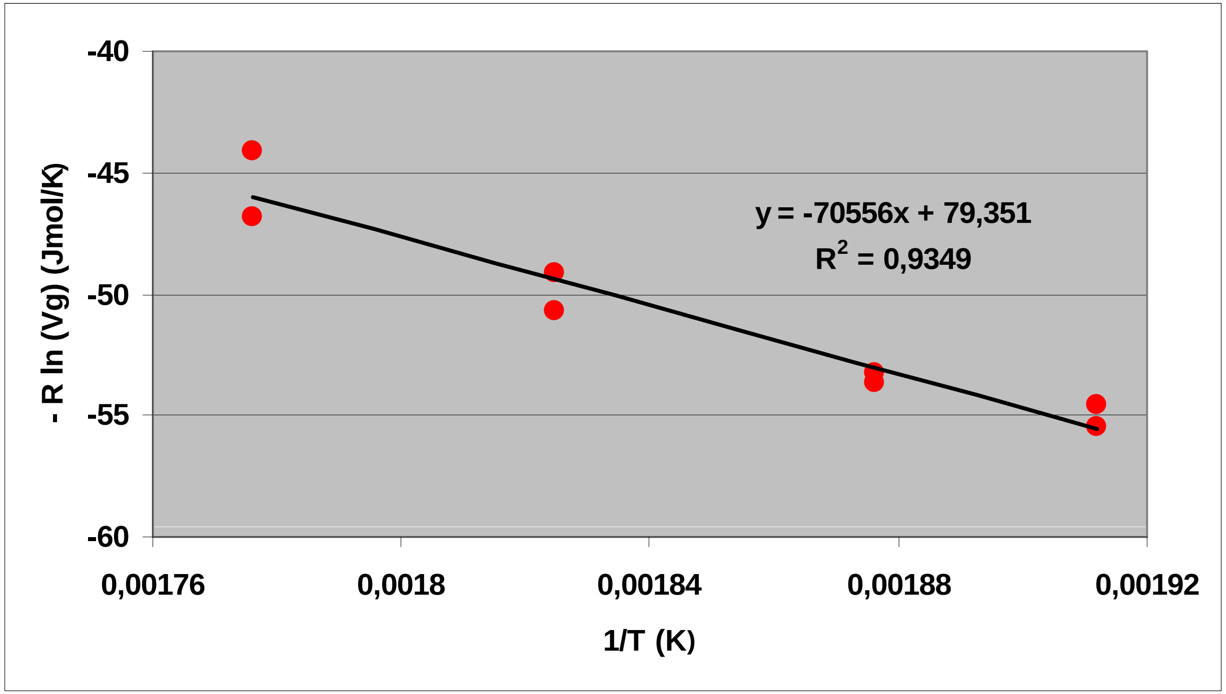


Eksperimental techniques :

Reversible binding by high temperature GC (200-400 ^oC)

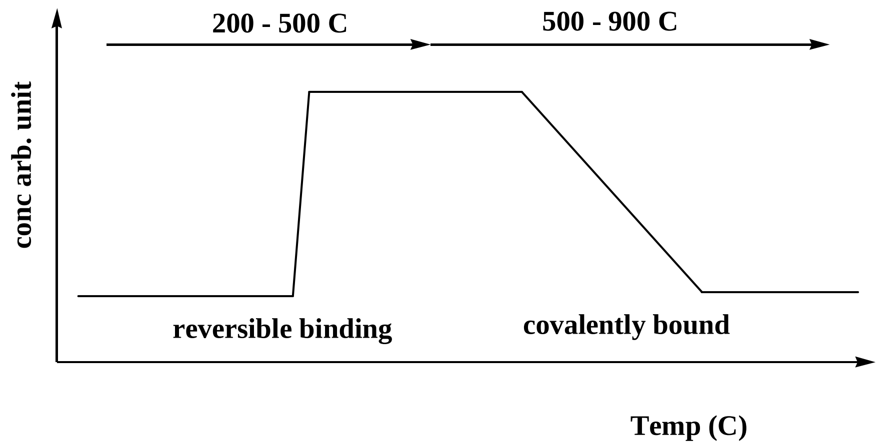
Covalent binding by dedicated oven systems

Low temperature binding of benzene to char



Adsorption enthalpy: -71 kJ/mol

Reactivity of char

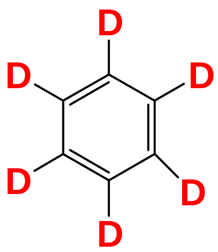


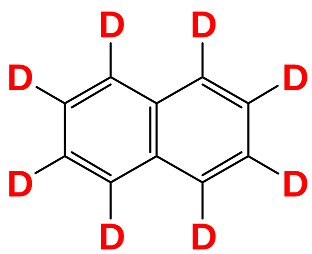
Eksperimental techniques :

Reversible binding by high temperature GC (200-400 ^{o}C)

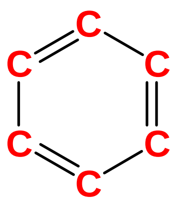
Covalent binding by dedicated oven systems

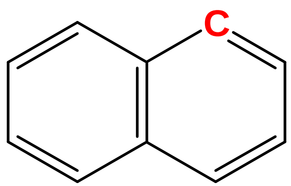
Stable isotope experiments





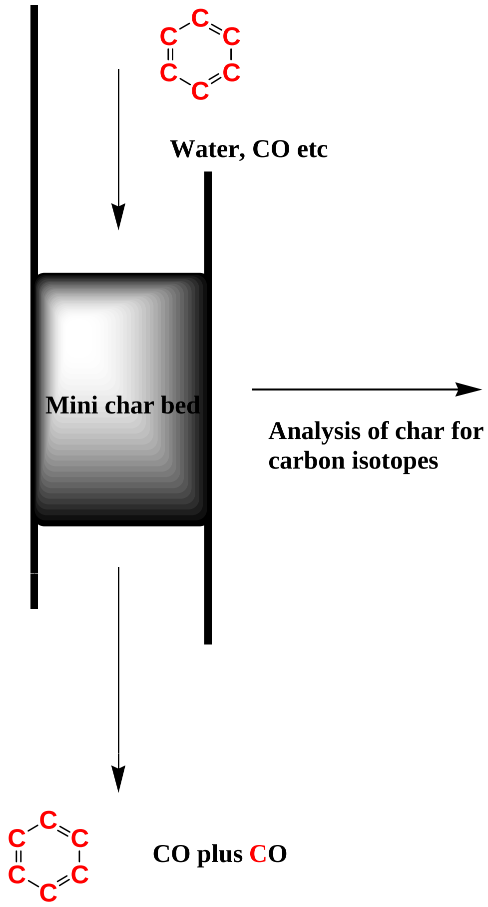
Deuterium labeling to study the presence of labile hydrogen's in char.





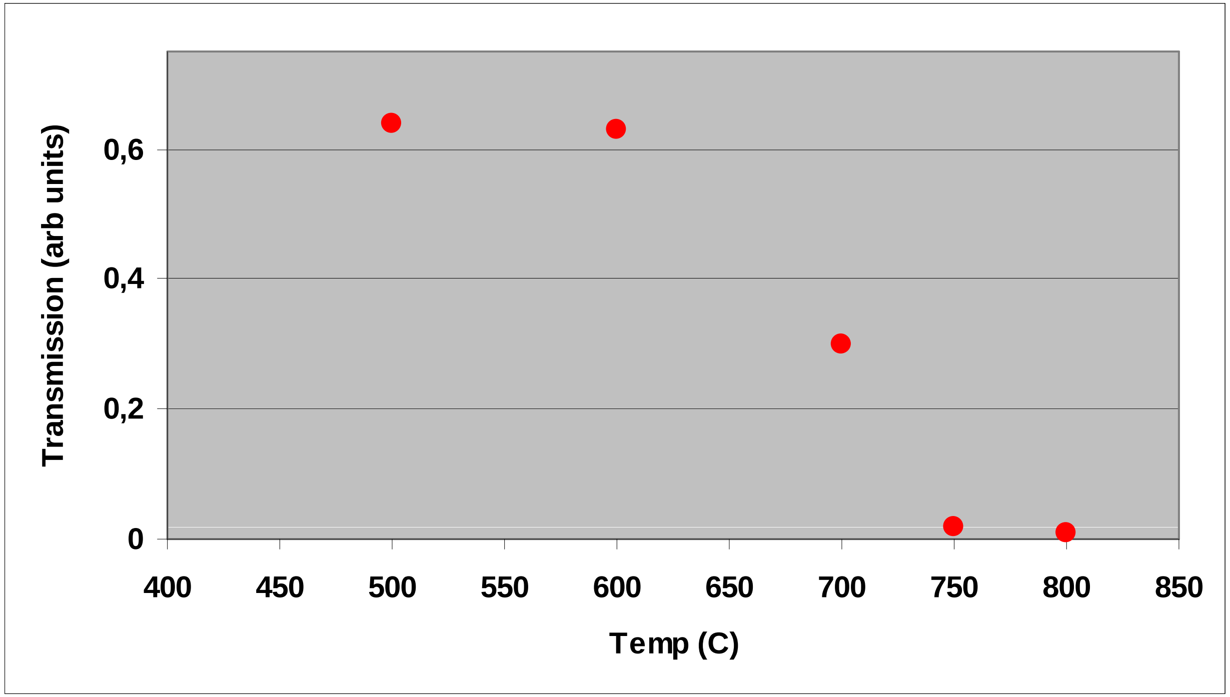
Carbon labeling to study the built up of carbon in char

Isotope studies with char



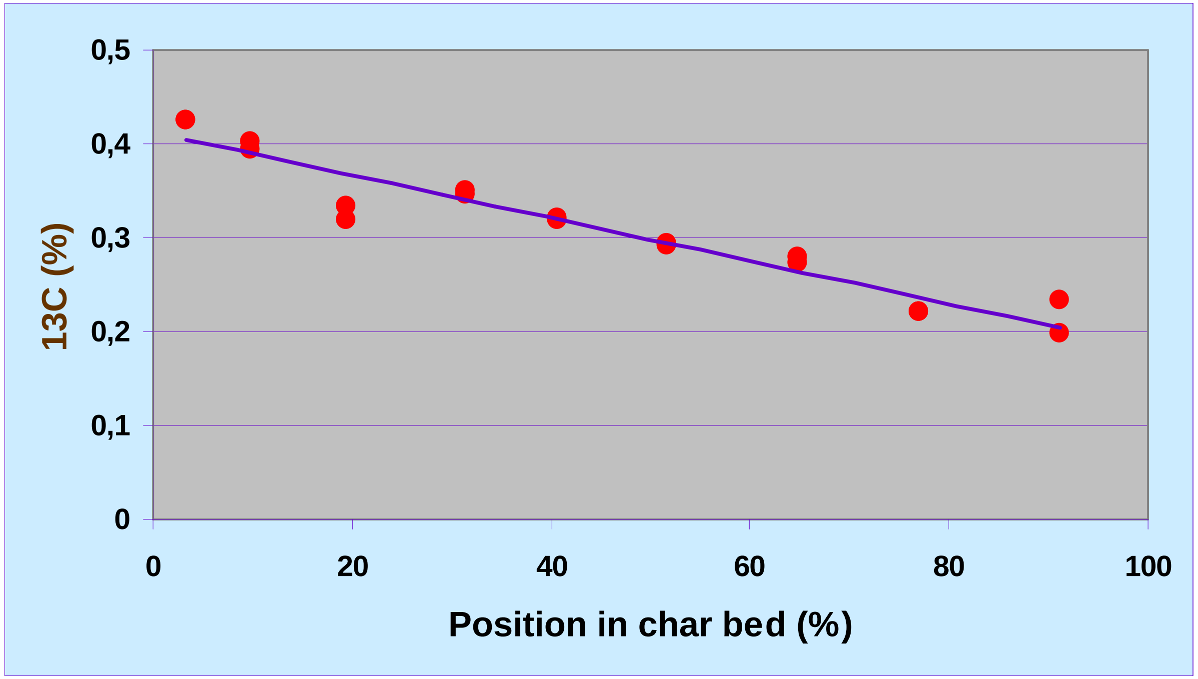
Analysis of exhaust for organic and isotope ratios

High temperature studies of char



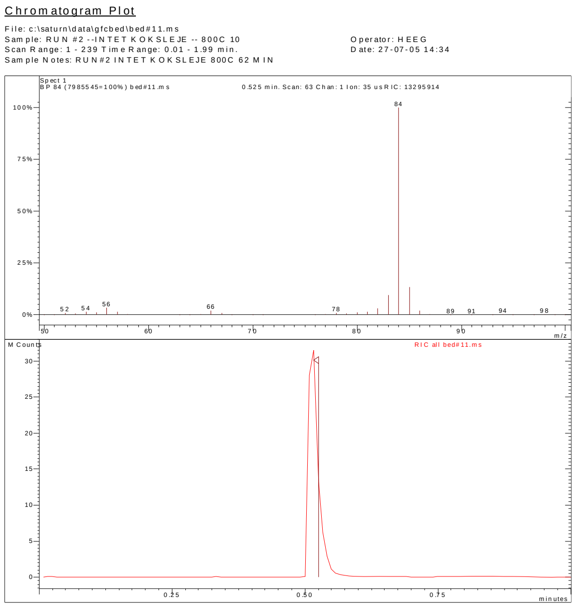
Transmission of benzene as function of temperature

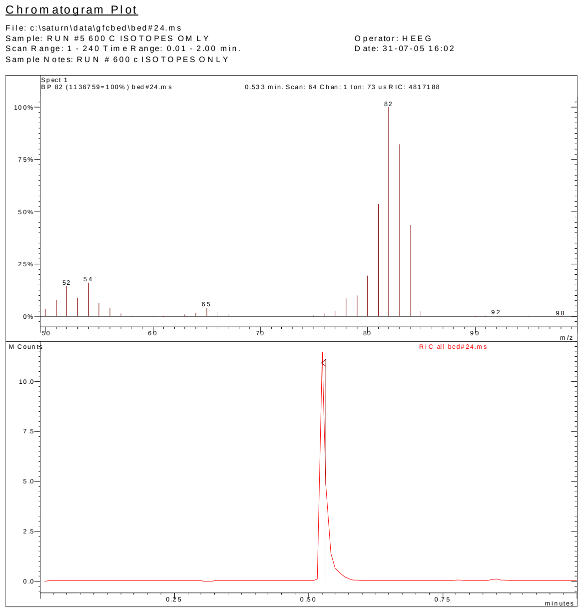
Carbon isotopes in char



Temperature 700 ^{o}C; transmission 35 %; char bound 50 %

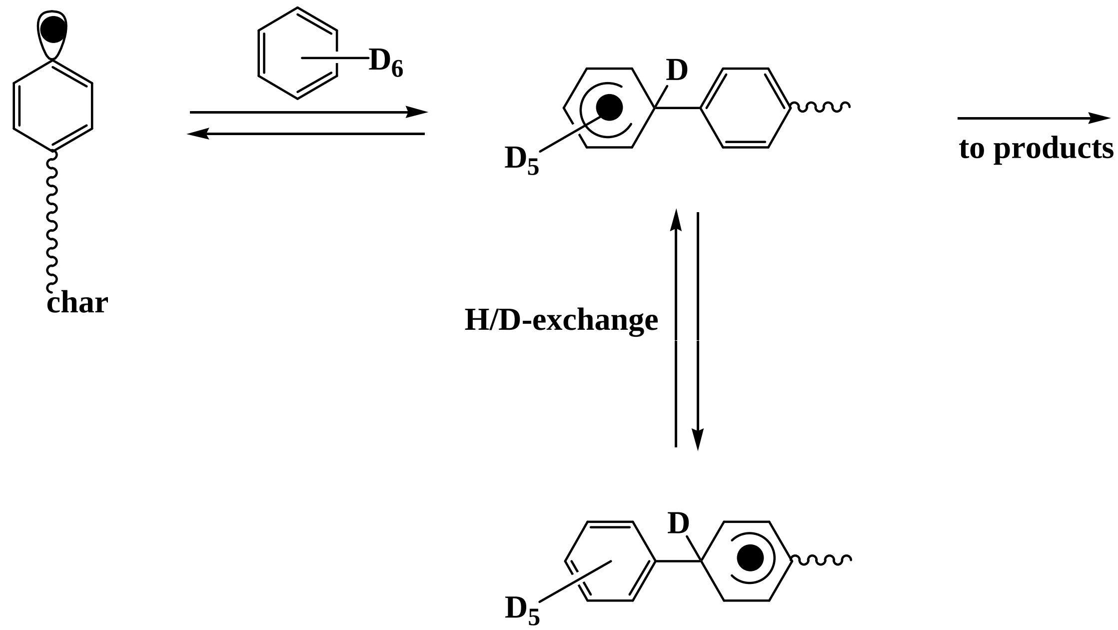
High temperature studies of char





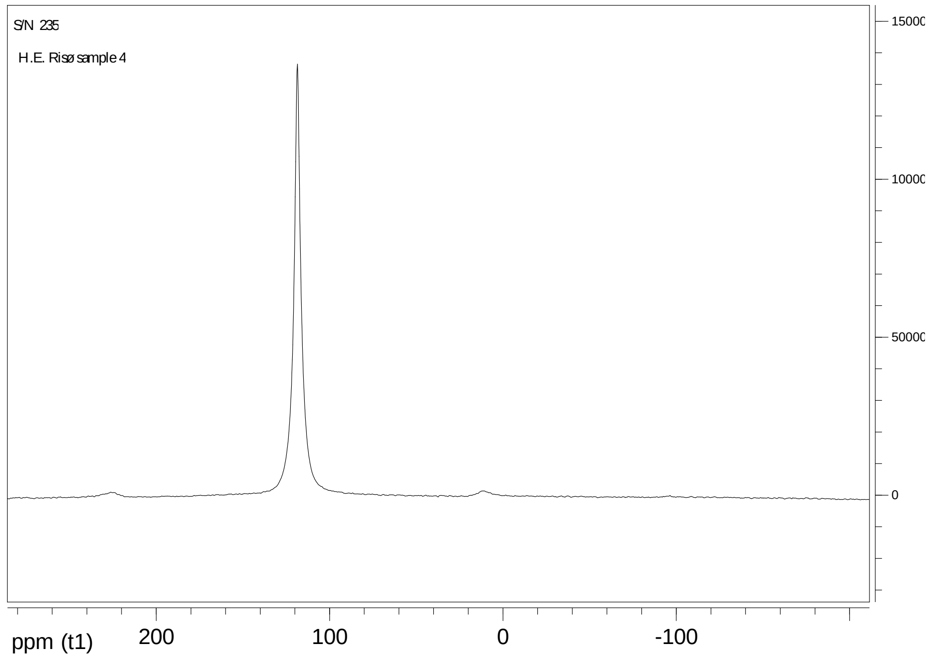
GC/MS analysis of D_6-benzene without char at 800 ^oC (left panel) and with char bed at 600 ^oC (right panel).

High temperature studies of char



Free radical mechanisms are most likely to account for the isotope exchange and binding.

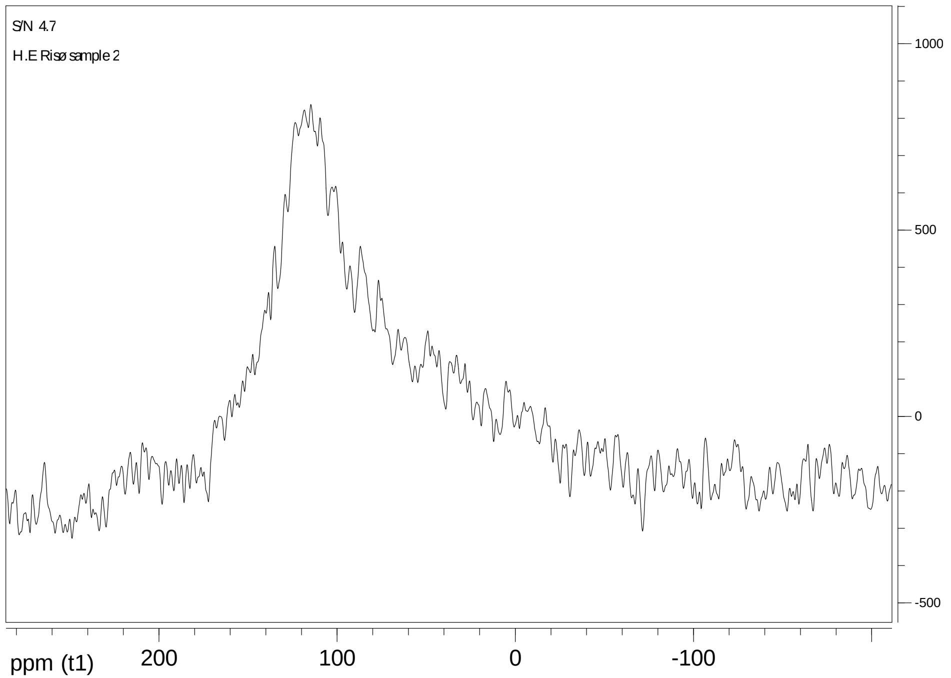
High temperature studies of char



^{13}C-solid-state NMR spectrum of char loaded with $^{13}C_6$-benzene at 200 °C

Solid-state NMR has been used to visualise the nature of char-bound benzene.

High temperature studies of char



^{13}C-solid-state NMR spectrum of char loaded with $^{13}C_6$-benzene at 800 °C

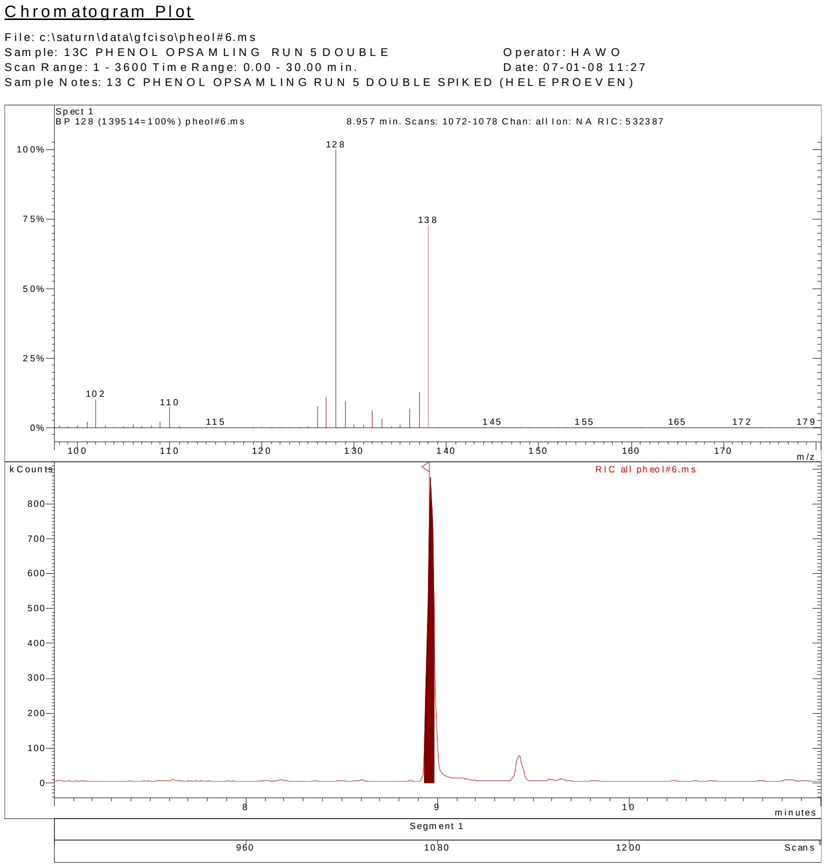
Solid-state NMR has been used to visualise the nature of char-bound benzene.

High temperature studies of char

Maintaining this covalently bound benzene/char system for additional 16 hours leads to a reduction of the solid-state NMR signal.

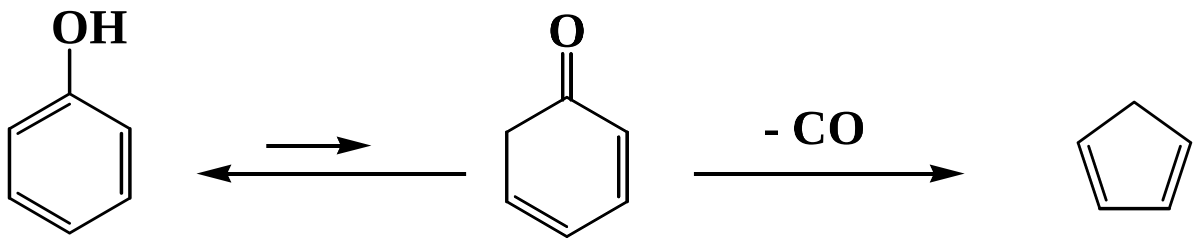
This is tentatively assigned the subsequent transformation of the covalently bound benzene into the rigid part of the char exhibiting longer relaxation times for the carbon nucleus and, hence, lower signal strength

High temperature chemistry of phenol



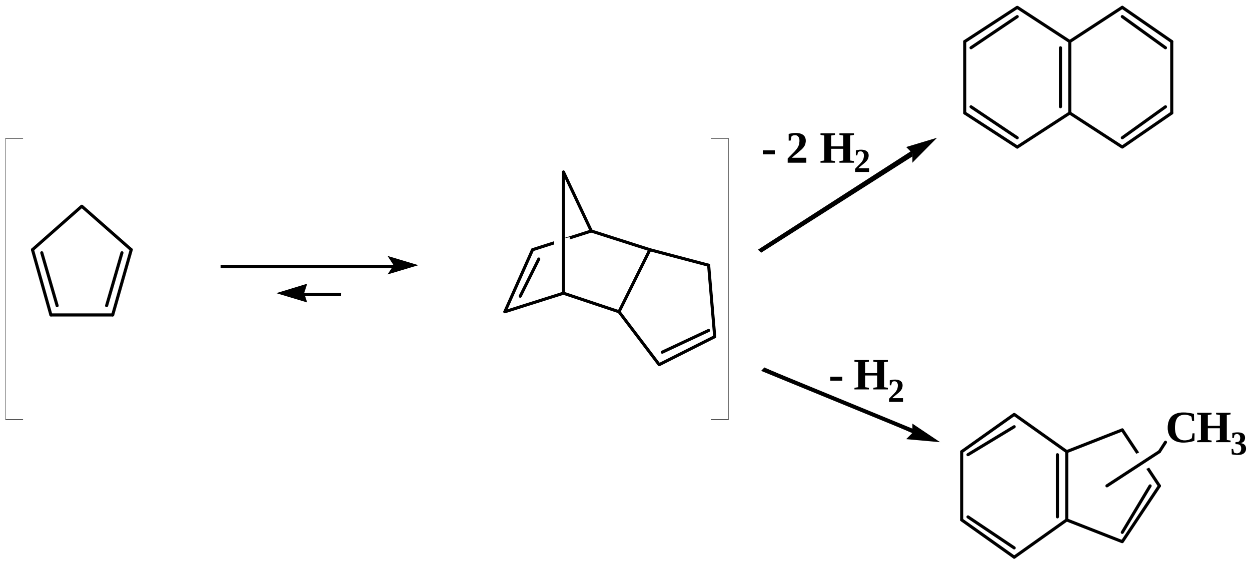
GC/MS analysis of naphthalene generated during loading of $^{13}C_6$-phenol at 800 °C. The sample is spiked with naphthalene (m/z 128)

High temperature chemistry of phenol



The rate determining step in the pyrolysis of phenol

High temperature chemistry of phenol



Formation of naphthalene and methylindenes

Gasification - The use of ^{13}C-labelled char

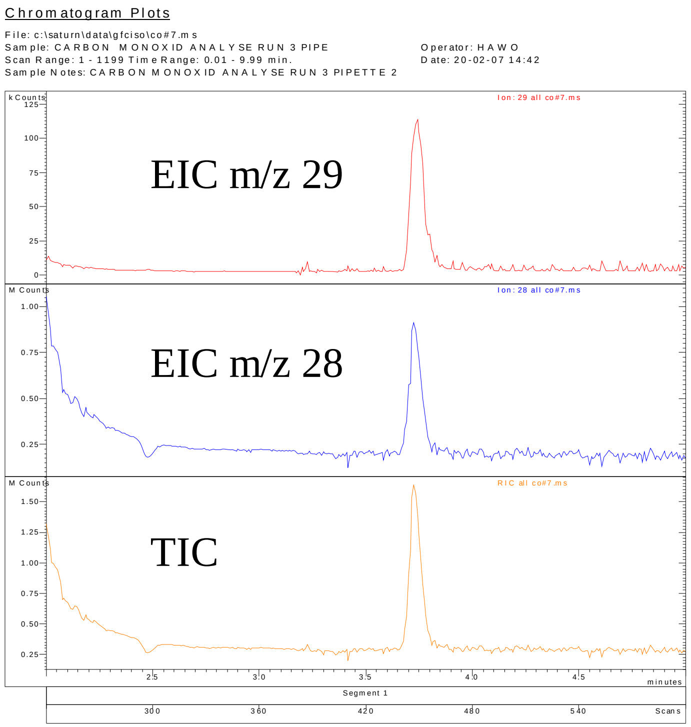
$$C + H_2O \rightleftharpoons CO + H_2$$

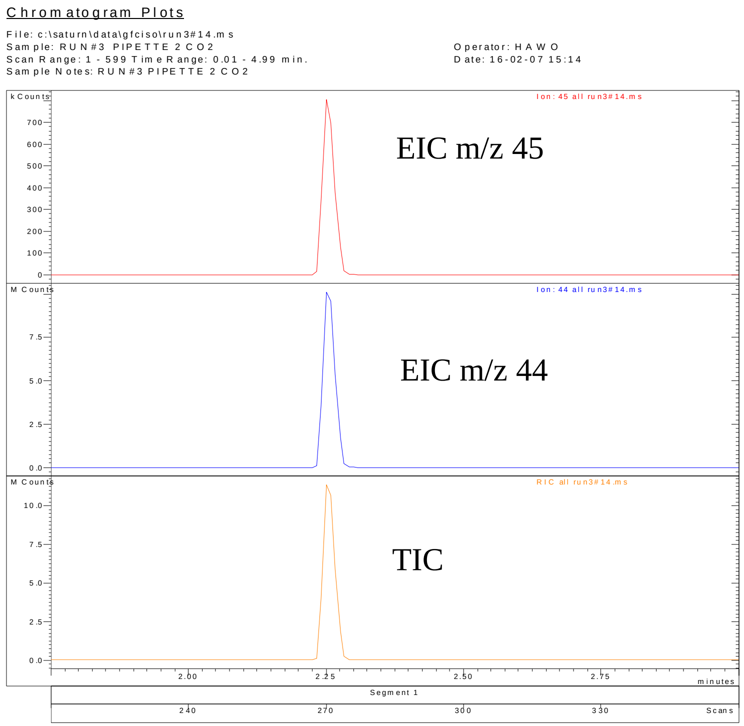
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

The gaseous products are formed as a result of a series of coupled reactions

Gasification - The use of ^{13}C-labelled char





Determination of ^{13}C abundance of carbon monoxide and carbon dioxide.

Conclusion – isotope study

**A trend in the binding efficiency, namely:
benzene < naphthalene < phenanthrene was found.**

Phenol behaved different from the other aromatic compounds studied. It partly undergoes decarbonylation leading to formation of naphthalene in a specific and well defined reaction pathway.

Isotope exchange reactions provided some evidence for a free radical mechanism as being responsible for the binding the compounds to the char bed.

Gasification of the labelled chars suggests that 95 % the incorporated carbon (benzene) loss its chemical history in the char bed.

From Biomass to Bio-char

Application of bio-char to soil has been proposed as a significant and long-term sink for carbon dioxide in terrestrial ecosystems.

An improved understanding of the mechanisms involved in bio-char application to soil is crucial in the ongoing debate about the addition of bio-char to soil to offset human-induced climate change.

Black is the new green

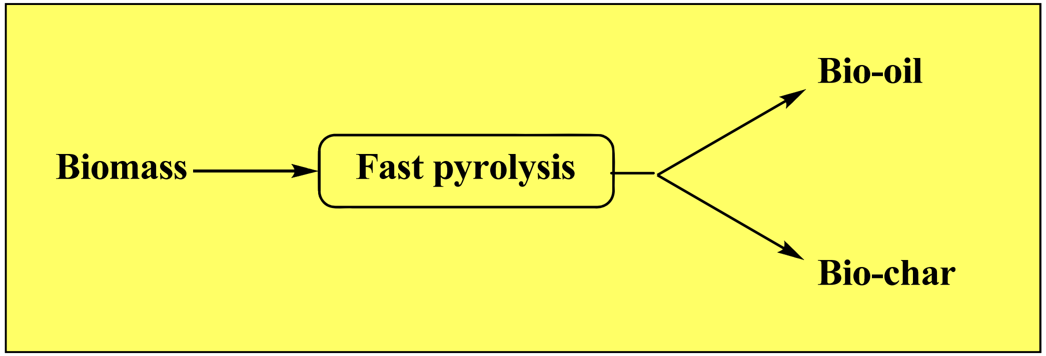
SEQUESTRATION **NEWS FEATURE** NATURE|Vol 442|10 August 2006

From Biomass to Bio-char

Bio-char is the carbon-rich product obtained by heating biomass at oxygen starvation and relatively low temperature (< 700 °C).

We are currently studying the co-production of bio-oil/bio-char based on wheat straw using an innovative fast pyrolysis centrifuge in the temperature range 475 – 575 °C and a residence time in the order 1 s.

N. Bech, N, K. Dam-Johansen, P.A . Jensen,.
Pyrolysis Method and Apparatus,
PCT Application WO 2006/117005, 2006.



Summary

We have developed methods for characterization of bio-char/bio-oil based on analytical flash pyrolysis in combination with GCMS.

These methods allow:

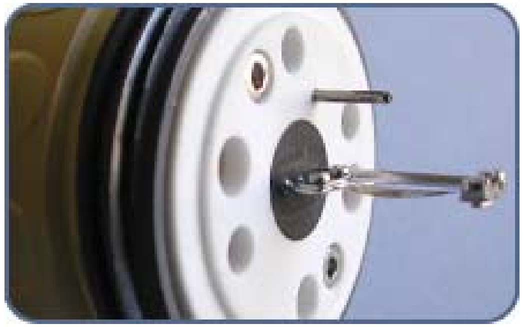
- ❑ Simulation of bio-oil composition
- ❑ Determination the origin of specific compound classes found in the bio-oil
- ❑ Determination of residual organic compound classes in bio-char

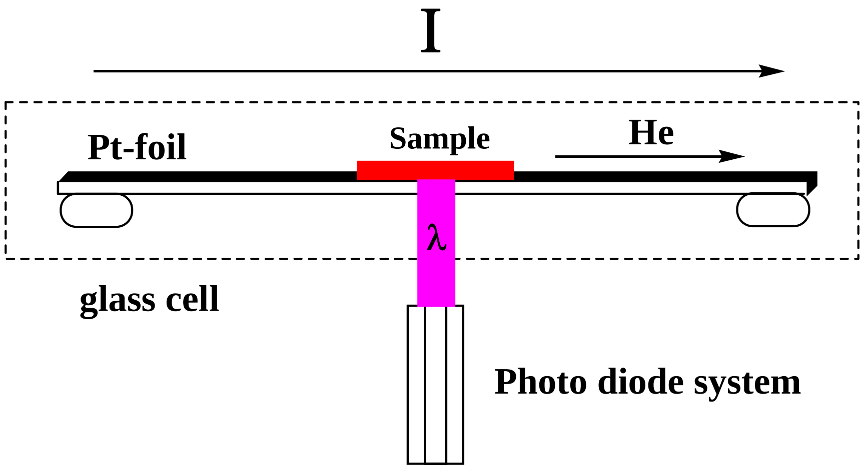
Analytical flash pyrolysis

Controlled fast heating is achieved by two DC pulses:

I. **30- 40 A for 5-10 ms**

II. **5-10 A for 1-2 s**

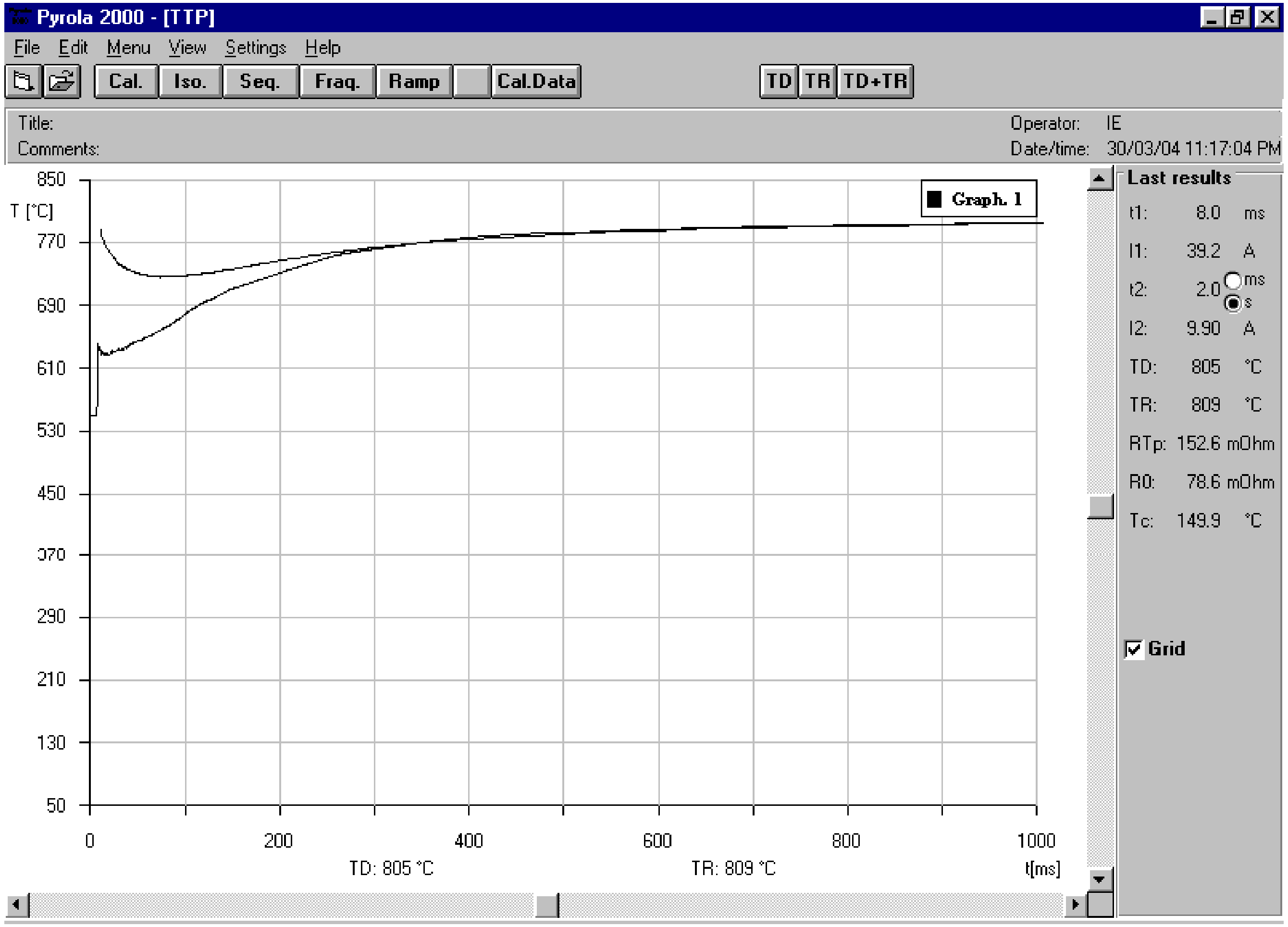




Ohmic heating using platinum foil (14 x 3 x 0.03 mm)

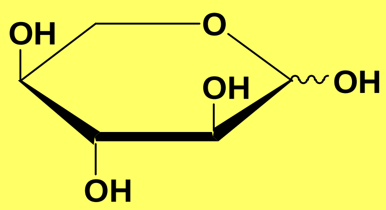
Instrumentation – Analytical flash pyrolysis

Process-near characterization

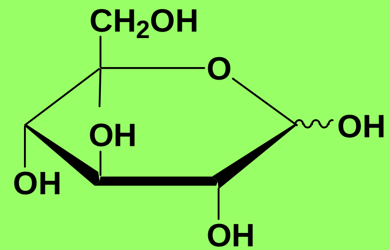


Biomass – dominant substructures

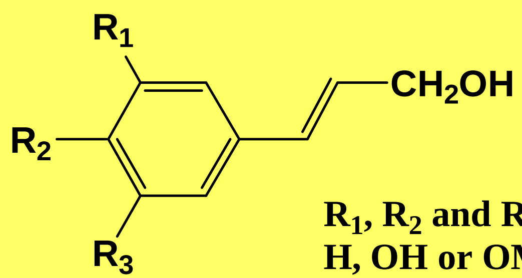
Hemi-cellulose



Cellulose

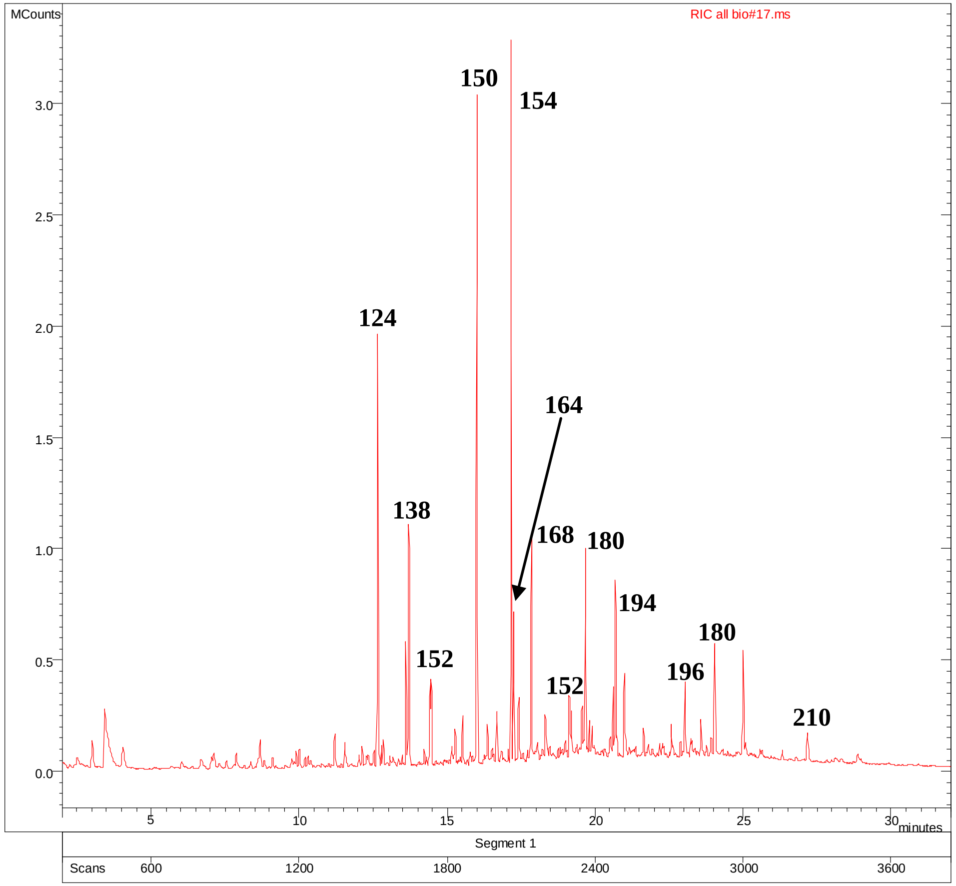


Lignin



R_1, R_2 and R_3 :
H, OH or OMe

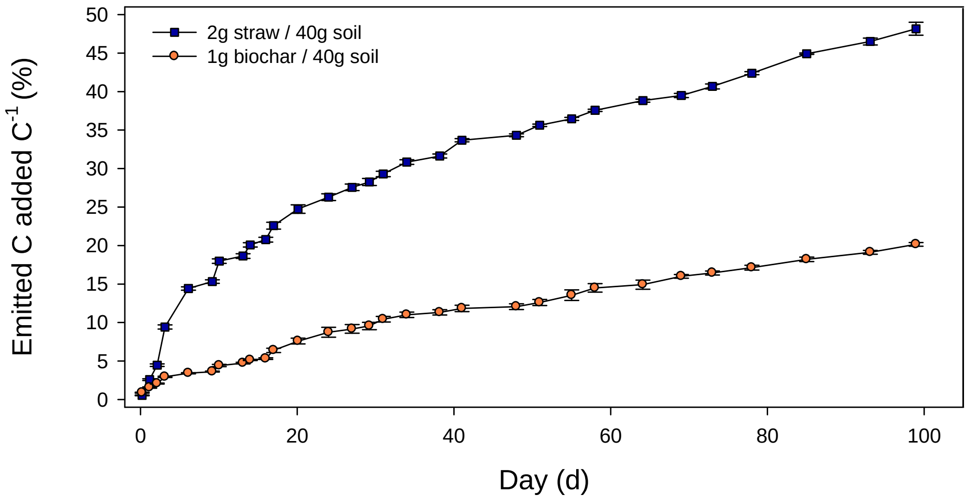
Analytical flash pyrolysis – Lignin

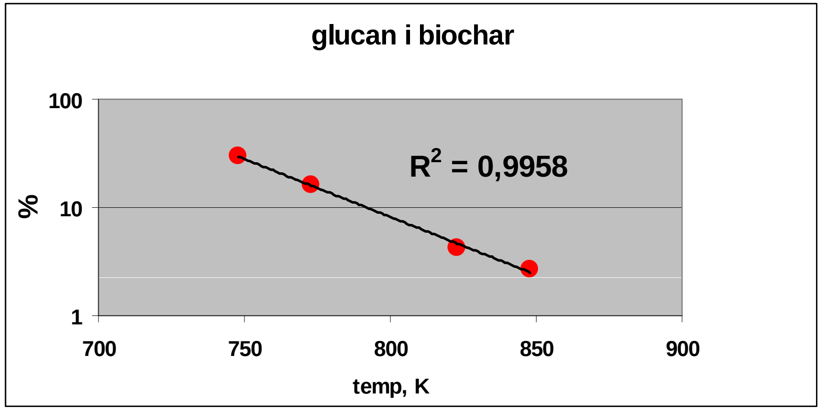


Analytical flash pyrolysis at 600 °C and 2 s of lignin

Backbone	H	Me	Et	$HC{=}CH_2$	HC=CHMe
Gu	124	138	152	150	164
Sy	154	168	182	180	194

Analytical flash pyrolysis – Bio-char





Investigation of the bio-availability of bio-char revealed that in the order 10 % of the carbon may be released as CO_2 in approximately100 days when bio-char is applied to soils.

Classical chemical methods indicates high concentrations of glucan in the bio-char, e.g. 10 - 2 % decomposing by a first order kinetics.

Conclusion

New methods for characterization of bio-char/bio-oil system have been developed:

- ✓ **Simulation of bio-oil composition by process-near methods**
- ✓ **Determination the origin of specific compound classes found in the bio-oil**

- ✓ **Determination of residual organic compound classes in bio-char**

Acknowledgements

Isotope study:

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Niels Bech
Norazana Ibrahim,
Peter A. Jensen